

Effect of substrate temperature and post-deposition annealing on the properties of evaporated CdSe thin films

E. Bacaksiz¹, B. M. Basol², M. Altunbaş¹, S. Yılmaz¹, M. Tomakin³, and B. Abay⁴

¹ Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

² SoloPower Inc., 1635 McCandless Drive, Milpitas, CA 95035, USA

³ Department of Physics, Rize Faculty of Arts and Sciences, Karadeniz Technical University, Rize, Turkey

⁴ Department of Physics, Faculty of Arts and Sciences, Atatürk University, Erzurum, Turkey

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1 Introduction

Cadmium selenide is a II–VI compound semiconductor with a band gap that has a good match with the solar spectrum. Electronic devices such as solar cells, thin-film transistors and detectors have been fabricated on thin films of CdSe [1–3]. The distribution of grain size and other structural and morphological properties of the films strongly affect the performance and reliability of active devices fabricated on such layers. Microstructural, electrical and optical characteristics of thin films are generally influenced by the nature of the substrate, growth conditions and post-deposition processing steps, if any. Grain growth may occur during film formation and/or during a subsequent heat-treatment step. The crystalline texture may also change during heat treatments in such a way as to minimize surface and interface energies. Some of the commonly used low-cost growth techniques for CdSe thin-film formation include close-spaced sublimation [4], electrodeposition [5], vacuum evaporation [6] and chemical bath deposition [7].

CdSe thin films deposited at relatively low substrate temperatures have attracted much interest in recent years [8–11]. It is known that the grain boundaries in polycrystalline CdSe thin films have a direct

* Corresponding author: e-mail: eminb@ktu.edu.tr

influence on the electrical properties of devices. It is also known that the grain boundary barrier height can be changed by modifying either the grain size or the trap level density by diffusing appropriate impurities along the grain boundaries.

In the work reported here, CdSe thin films were first grown on glass substrates kept at or below room temperature and then annealed at elevated temperatures. Effects of the growth and post-deposition anneal temperatures on the film properties such as grain size, texture, resistivity and optical band gap were studied to see which of these process conditions were more effective determining the film properties and to establish a correlation between the process parameters and the film properties.

2 Experimental

CdSe thin films were deposited by vacuum evaporation at a vacuum level of 3×10^{-2} Pa on soda-lime glass substrates at controlled temperature [12]. The vacuum apparatus consisted of a quartz-lined graphite chamber and included a heated source bottle, a quartz filter over the source bottle to act as a diffuser and a substrate holder placed 8 cm above the quartz filter. Substrates were clamp-mounted onto the holder face down and they had a direct view of the quartz filter. Source and substrate holder temperatures were monitored and controlled separately using thermocouples. The substrate thermocouple was placed at the holder/substrate interface. The substrate holder was cooled using liquid nitrogen while a secondary heater was used to adjust its temperature in the range 100–300 K. The evaporation rate of the source material was controlled by the source temperature.

The films were grown at substrate temperatures of 100, 200 and 300 K using CdSe powder as the source material. The growth rate was controlled by the source temperature and was about 1.5 nm/s. The final thickness of the films was nominally 2000 nm. After deposition, the layers were annealed at 200, 300 and 400 °C for 30 min in an air oven. X-ray diffraction (XRD) data were collected using a Rigaku D/Max-IIIC diffractometer with Cu K_{α} radiation over the range $2\theta = 3-70^{\circ}$ at room temperature. Morphological information was obtained using a scanning electron microscopy (SEM)/focused ion beam instrument manufactured by FEI. The absorption spectra of the films were recorded using a Perkin–Elmer Lambda 2SUV/Vis spectrometer in the wavelength range 190–1100 nm using non-polarized light. Resistivity values were determined by the standard four-point method at room temperature.

3 Results and discussion

Figure 1a–c show the XRD spectra of CdSe films deposited on glass sheets at substrate temperatures of 100, 200 and 300 K, respectively. As can be seen, the textures of all the films are hexagonal with a strong (002) preferred orientation. The peak positions are at $2\theta = 25.86^{\circ}$, 25.72° and 25.66° corresponding to lattice parameters, c , of 0.688, 0.692 and 0.693 nm, respectively, for the films grown at 100, 200 and 300 K. The value of the lattice parameter for the films produced at low substrate temperatures is less than that of a powder sample (0.701 nm) [13], suggesting that these films may be subjected to stresses in the plane of the substrate surface. The origin of the stress may be the difference in the linear thermal expansion coefficients of CdSe ($\alpha = 7 \times 10^{-6}/\text{K}$) and soda-lime glass ($\alpha = 9 \times 10^{-6}/\text{K}$). The gradual increase of the lattice parameter towards the powder value with increasing substrate temperature suggests that stress is partly relieved as the substrate temperature is increased during film growth. The intensity of the (002) peak increases as the substrate temperature increases, indicating improved crystallinity and a gradual increase in the preferential orientation.

The full width at half maximum (FWHM) of the hexagonal (002) peaks was calculated from the data of Fig. 1. It was found that the FWHM decreased from 0.235° to 0.177° as the substrate temperature increased from 100 to 300 K. The grain sizes were calculated from the Scherrer relation:

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

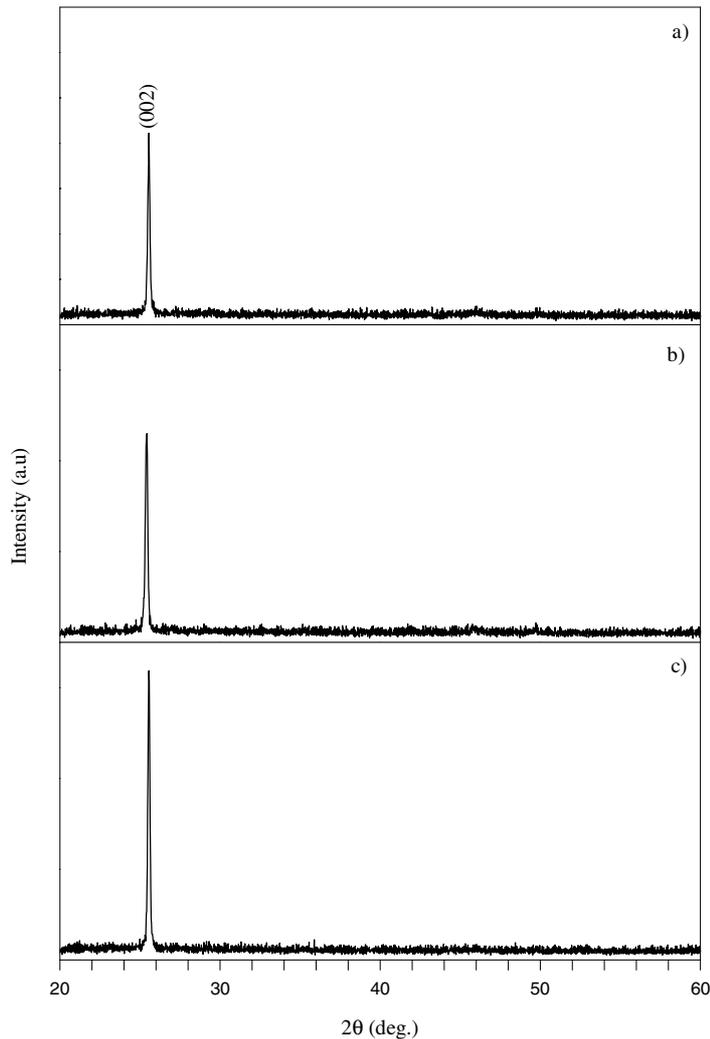


Fig. 1 XRD diffraction patterns of CdSe thin films grown at three substrate temperatures: a) 100 K; b) 200 K; c) 300 K.

where D is the grain size and β is the FWHM. The calculated grain size was about 34 nm for the film grown at 100 K, whereas a grain size of about 46 nm was found for the layer processed at the substrate temperature of 300 K. Although the actual grain size values could not be confirmed, this trend is in agreement with the SEM data, as discussed later.

Figure 2a–c shows a series of XRD spectra taken from a film deposited at 100 K and then annealed for 30 min at 473, 573 and 673 K, respectively. As can be seen, the strong (002) preferred orientation of the as-deposited film is preserved as the annealing temperature is increased, and the intensity of the (002) peak gradually increases with increasing annealing temperature. Here, it should be mentioned that the samples that were deposited at $T_s = 200$ and 300 K and then annealed at elevated temperatures showed a trend that was similar to the data of Fig. 2; however, the post-annealing increase observed in the XRD peak intensity for the film grown at 300 K was only minimal. Referring back to Fig. 2, the peak positions for the as-deposited CdSe film and the film annealed at 673 K are $2\theta = 25.86^\circ$ and 25.48° , respectively, corresponding to lattice parameter values, c , of 0.688 and 0.700 nm. This increasing trend in c upon

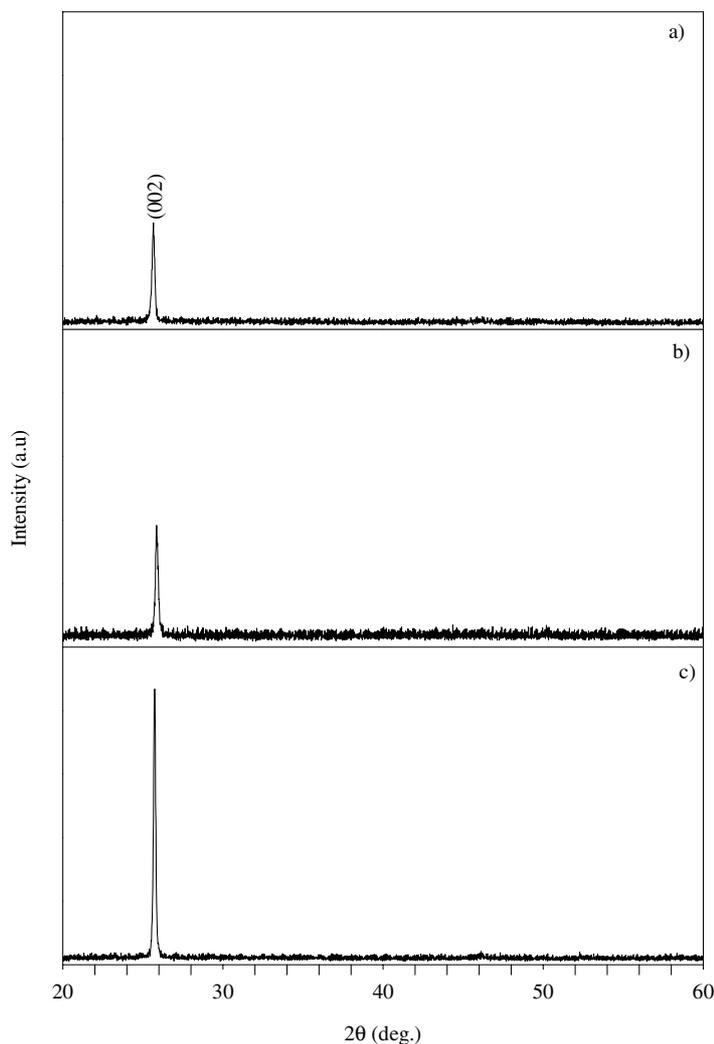


Fig. 2 XRD diffraction patterns of CdSe thin films grown at 100 K and annealed at: a) 473 K; b) 573 K; c) 673 K.

annealing indicates that during the post-deposition annealing step, stress in the film may be relieved and therefore the c value approaches that of the CdSe powder sample [13]. It should also be noted that the grain sizes of the samples produced at a substrate temperature of 100 K and then annealed at 673 K slightly increased from 34 to 40 nm upon annealing, as calculated from the Scherrer equation. However, the film deposited at a substrate temperature of 300 K had almost the same grain size after annealing at 673 K.

SEM images of the films deposited at substrate temperatures of 100, 200 and 300 K are shown in Fig. 3. Although the morphology of the film deposited at 200 K may suggest a somewhat larger grain size compared to the film deposited at 100 K, the morphological change is much more apparent for the film deposited at 300 K. However, it is not possible to assign specific grain size values to these films looking at their surface morphologies. In general the morphology observed suggests a larger grain size for the sample grown at the higher substrate temperature. This is in line with the grain size calculations made using the XRD data.

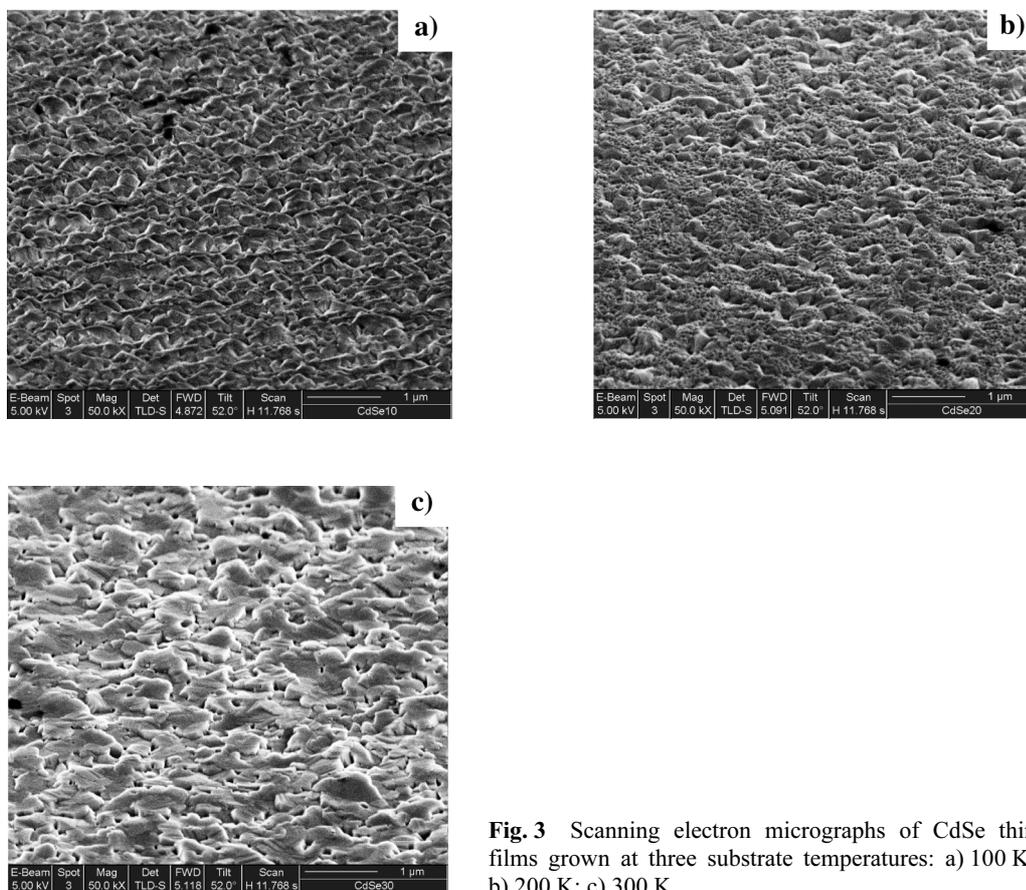


Fig. 3 Scanning electron micrographs of CdSe thin films grown at three substrate temperatures: a) 100 K; b) 200 K; c) 300 K.

Figure 4 shows SEM images of the film deposited at a substrate temperature of 100 K and then annealed at temperatures of 473, 573 and 673 K. As can be seen from these micrographs the morphology of the CdSe films did not change much upon annealing in air even at 673 K for 30 min. These results are similar to those for films grown at substrate temperatures of 200 and 300 K. In all cases, although the grain size did not seem to change appreciably, the surface features changed slightly from more faceted to more rounded after annealing at 673 K. It appeared that some necking and intergrain fusing were initiated at 673 K. Since the grain size did not change but the lattice parameter changed upon annealing, we can conclude that, in terms of effects on structural properties, the role of the post-deposition heat-treatment step was to release the stress in the layers.

The optical band gap values of the films were obtained from optical transmission measurements and by plotting $(\alpha h\nu)^2$ values as a function of energy, $h\nu$. Figure 5 shows data obtained for CdSe films deposited at substrate temperatures of 100, 200 and 300 K. As can be seen, two different linear regions appear in the graphs indicating two different band gap energy values for each sample. The larger of the two direct band gap transitions (E_{g1} , E_{g2}) is thought to be due to the spin orbit splitting of the valance band [14]. The inset of Fig. 5 expands the data collected near the band edge to resolve better the band gap values.

From the inset of Fig. 5, the extrapolated values of the optical energy gap E_{g1} are 1.68, 1.68 and 1.71 eV for films deposited at substrate temperatures of 100, 200 and 300 K, respectively. As can be seen from these data, the absorption edge is shifted towards higher energy values approaching the value for single-crystal CdSe [15]. The increase in the band gap energy with increasing substrate temperature can be attributed to a shift in stoichiometry which is encountered in the work of Mondal et al. [14].

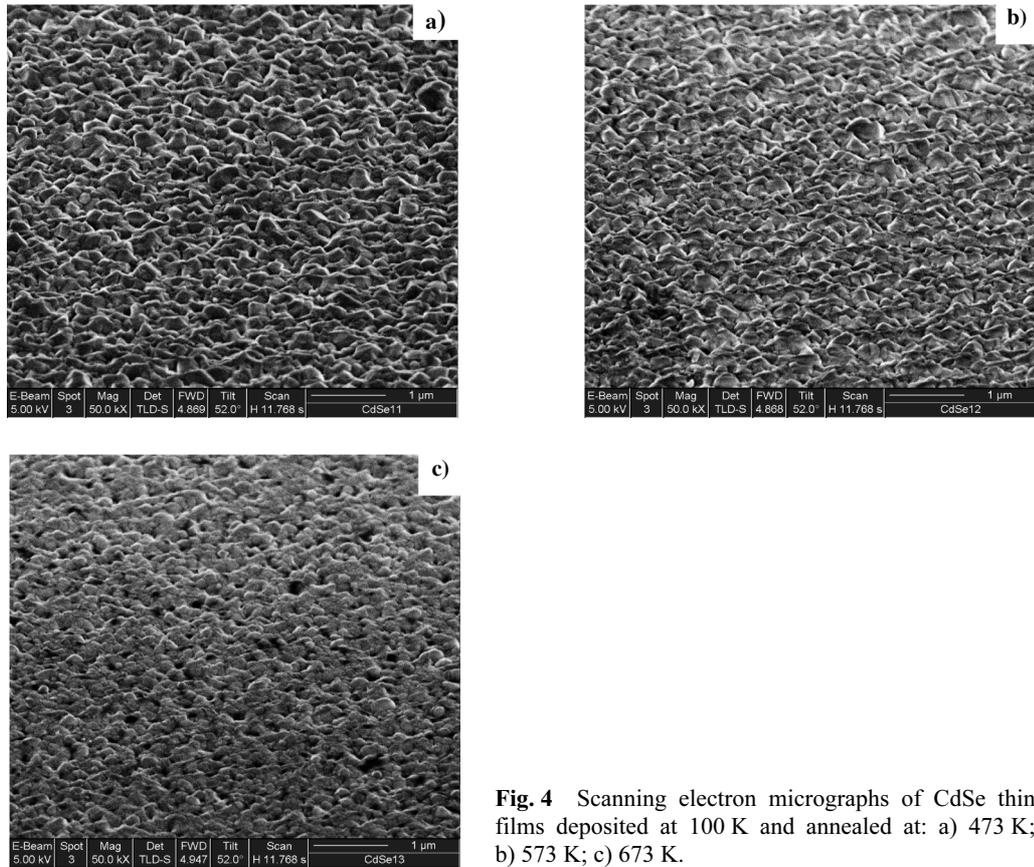


Fig. 4 Scanning electron micrographs of CdSe thin films deposited at 100 K and annealed at: a) 473 K; b) 573 K; c) 673 K.

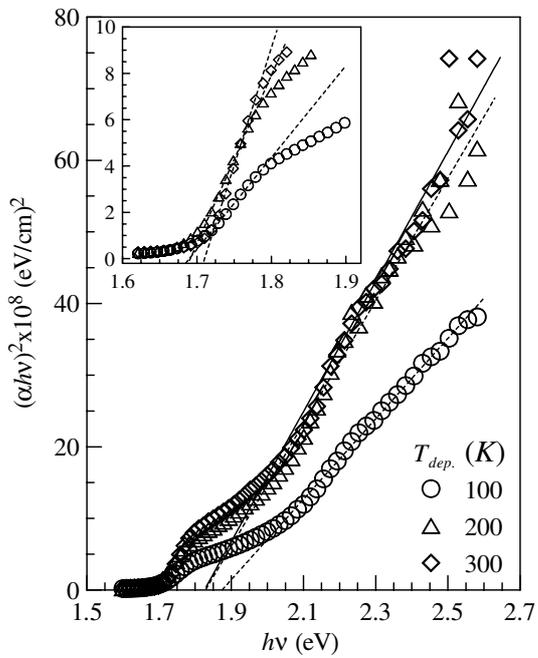


Fig. 5 Absorption spectra data of CdSe thin films grown at three different substrate temperatures.

The E_{g2} value was found to be between 1.87 and 1.83 eV, with higher substrate temperatures during growth yielding smaller E_{g2} values. Velumani et al. [16] have reported that the energy band gaps, E_{g1} and E_{g2} , for CdSe films decrease with increasing substrate temperature. Also, they reported that strain decreases and grain size increases with higher substrate temperature. The energy gap E_{g1} is in good agreement with the results of Mondal et al. [14], but our E_{g2} value is lower than their reported value of 1.91 eV. Similar band-splitting transitions in CdSe thin films have been reported in the literature [17, 18]. The work of Lalitha et al. [19] showed that CdTe films have two direct transitions at $E_{g1} = 1.48$ eV and $E_{g2} = 1.78$ eV, when the grain size was about 80 nm. Theoretical calculations by Cardona et al. [20] showed that the second direct transition is due to spin-orbit splitting of the valence band, which results in an additional transition from the higher valence level.

The effect of post-growth heat treatments on the band gap of a CdSe film deposited at a substrate temperature of 100 K is shown in Fig. 6. The energy band gaps, E_{g1} , obtained from the inset in Fig. 6 were found to be approximately 1.68 eV for the samples annealed at 475, 573 and 673 K. It is noted from the SEM studies that the annealing process did not cause much difference in the grain size, thus causing no appreciable change in the E_{g1} value. It is interesting to note that although the E_{g1} values did not change, the E_{g2} values were found to change from 1.87 eV (as-deposited film) to 2.25 eV upon annealing. The data of Fig. 6 also show a sharper band edge for the annealed samples. Similar trends in E_g values were observed upon annealing the films deposited at substrate temperatures of 200 and 300 K. The constancy of E_{g1} upon annealing in our work is supported by the SEM results and the almost unchanged grain size.

The resistivity of the film deposited at 100 K was found to increase from 1.6×10^6 to $8 \times 10^7 \Omega \text{ cm}$ upon annealing at 673 K. This trend was also observed for the films produced at 200 and 300 K. The observed increase in the resistivity may be attributed to the possible formation of an oxide whose existence could not be detected from the XRD data. Additionally, chemisorption of oxygen at the grain boundaries is expected to reduce n-type nature of the grain boundary regions, increasing the barrier height and thereby increasing the measured effective resistivity value. It should be noted that annealing in an oxygen-containing atmosphere is a technique that is commonly used to convert thin CdTe layers from n-type to p-type [21]. Therefore, oxygen has acceptor quality in II-VI compounds and may cause compensation at the grain boundaries of CdSe films raising the barrier to electron transport.

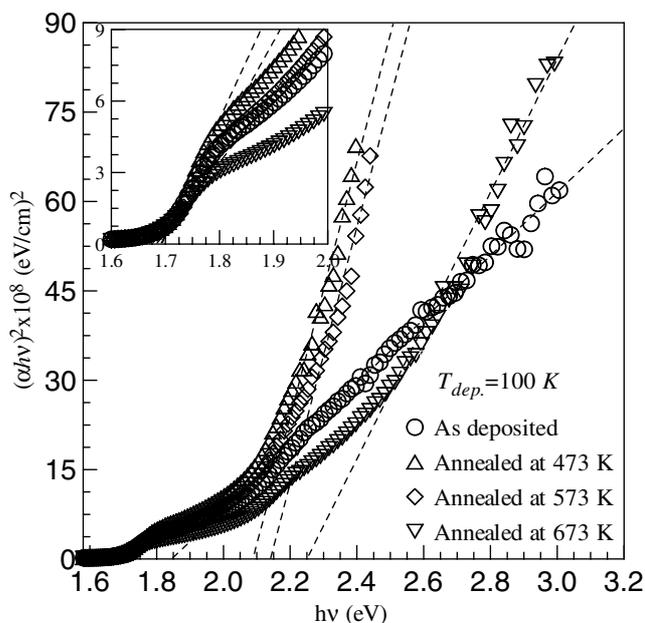


Fig. 6 Absorption spectra data of CdSe thin films deposited at 100 K and then annealed at three different temperatures.

4 Conclusions

We have studied the structural, optical and electrical properties of evaporated CdSe thin films as a function of the substrate temperature during growth and the post-deposition annealing temperatures. It was observed that as-grown CdSe thin films had a hexagonal wurtzite structure with a preferred orientation along the (002) direction irrespective of the substrate temperature. Post-deposition anneals did not affect the predominant (002) crystallographic texture. Only the degree of preferred orientation was enhanced as the annealing temperature was increased. SEM studies showed that the grain size of CdSe thin films did not change on annealing at elevated temperatures. However, annealing at 673 K initiated intergrain coalescence and fusing and altered surface morphology reducing faceting. From optical transmittance measurements, two direct optical transitions corresponding to band gaps of 1.68 eV (E_{g1}) and 1.83 eV (E_{g2}) were observed for films deposited at substrate temperatures of 100 K. As the annealing temperature was increased, the band gap E_{g1} did not change, but E_{g2} increased from 1.83 to 2.25 eV. Resistivity measurements indicated that annealing at 673 K in air formed a highly resistive compensated CdSe film.

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